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MODELING STRATEGY FOR NETWORKS WITH BOTH STEPWISE AND CHAINWISE MECHANISMS: AMINE-EPOXY CHEMISTRY WITH ETHERIFICATION

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ABSTRACT

A comparison between the entirely statistical and the combined kinetic and statistical models for amine-epoxy networks, both studied previously in the literature is made. The chemistry studied involves the generation of a secondary site, which reacts in the network through chainwise addition, rather, than the stepwise addition mode of the primary reaction. It is shown that the combined model (Bokare and Gandhi, 1980) is exact and the random model (Bidstrup, 1986; Riccardi and Williams, 1986; and Tsou and Peppas, 1988) is approximate. The assumptions underlying the two models are delineated. It is shown that under certain circumstances the predictions of the two models can differ by several hundred percent. Further the combined model is extended to predict the postgel properties of the network.
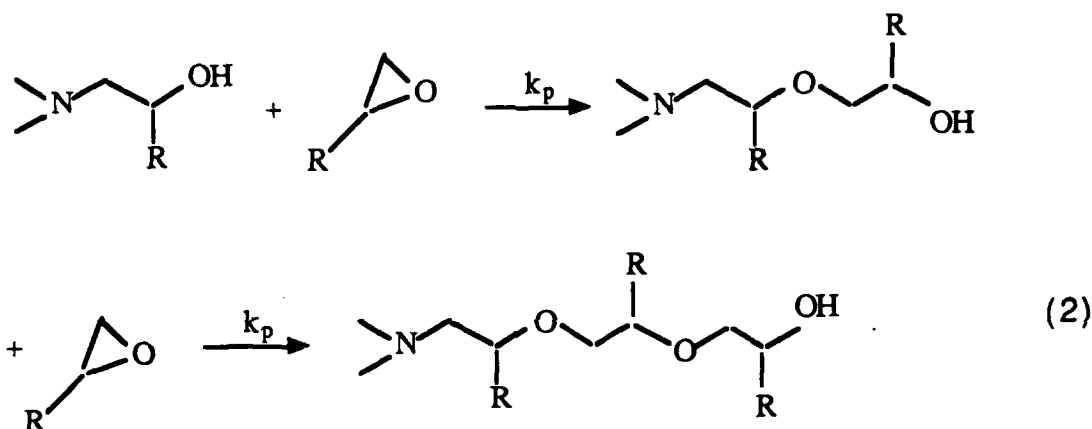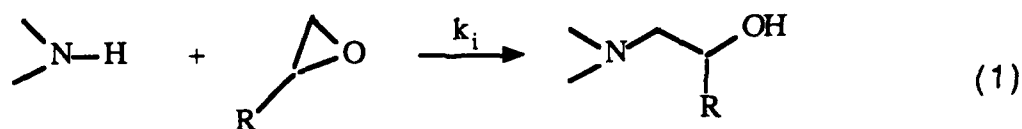
INTRODUCTION

Application of the classical Flory-Stockmayer[1] theory for polymer growth, and that of its several other manifestations[2,3], is contingent upon the reactants meeting certain conditions. These conditions have been well discussed[4] and ensure that the reaction probability between any two sites is random. Deviations from the the classical paradigm, include, chainwise reactions[5], unequal reactivity[6], substitution effects[7], and cyclization in finite species[8]. Given a well established chemistry it is possible to account for these non-idealities, at least, to some degree of approximation[9]. The present paper is concerned with the non-ideality introduced by chainwise side reactions in stepwise systems.

The chainwise reaction is conditional upon the initiation step. Further non-random complications appear due to termination, chain transfer reactions and diffusion limitations[10,11]. "Living" anionic polymerization is the simplest case of chainwise chemistry[11]. Here the reaction between two sites is conditional only upon one of the sites having been initiated. Dusek and Somvarsky[12] have analyzed this network model chemistry and shown the nature of the deviations.

Consider the linear polymer case in homogenous growth conditions. In stepwise systems, if we neglect the last three non-idealities mentioned above, the chain lengths have a geometric distribution. In contrast, if the reaction mechanism is "living" anionic, and the initiation step is instantaneous, the chain lengths have a Poisson distribution[13].

This work explains the modelling strategy, where both the stepwise and chainwise mechanisms are operative. Specifically, we apply these results to the amine-epoxy chemistry. This chemistry has been well studied in the literature[14-16] and several workers[17-21] have developed network models. The reaction between the amine hydrogen and epoxy (1) is usually the main reaction. However, the hydroxyl unit generated on the epoxy can further react with another epoxy (2) to continue the chain growth. This secondary reaction is like "living" anionic polymerization[17,22]. For this reaction the amine acts as an initiator and the epoxy-hydroxyl reaction is the conventional propagation step. However, in usual amine-epoxy networks, the amines are stoichiometrically in balance with the epoxies and the propogation step is much slower than the initiation step. This

could have led some workers[18-20] to ignore the chainwise nature of the side reaction. Their models are therefore approximations to the chemistry they assume. Previous work by Bokare and Gandhi[21] accounts for the chainwise nature of the side reaction. Dusek[17] has also presented a model faithful to this chemistry in the limit of slow propogation step.

$$\begin{array}{c}
\text{>N—H} + \triangle\text{O} \xrightarrow{k_i} \text{>N} \diagup \text{OH} \\
\end{array} \quad (1)$$

$$\begin{array}{c}
\text{>N} \diagup \text{OH} + \triangle\text{O} \xrightarrow{k_p} \text{>N} \diagup \text{O} \diagup \text{OH}
\end{array}$$

$$+ \triangle\text{O} \xrightarrow{k_p} \text{>N} \diagup \text{O} \diagup \text{O} \diagup \text{OH} \quad (2)$$

We shall compare the modelling assumptions inherent in past modelling strategies. In route, we shall develop a gen· ·a. framework for growth models of networks with both stepwise and chainwise reactions. We shall also explain the chemical situations under which the deviations due to chainwise reaction are pronounced. Finally a model for calculating post-gel properties for such networks shall be presented.

For reasons of comparison and mathematical ease we have restricted the analysis to amine-epoxy networks. Similar considerations hold in other important chemistries like, epoxides and alcohols[23,24], epoxides and carboxylic acids, isocyanates and alcohols, isocyanates and amines.
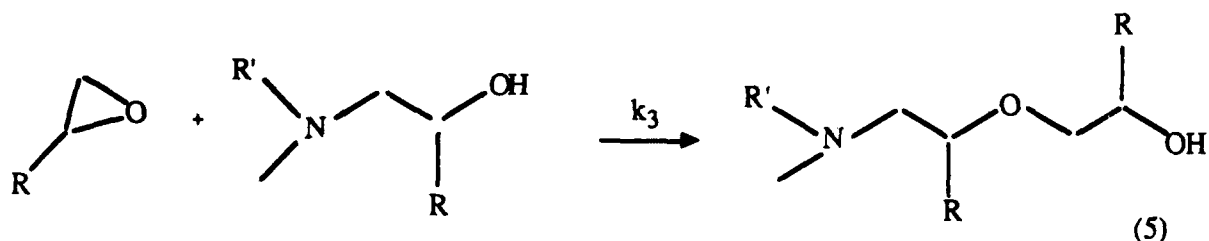
CHEMISTRY

Any model for network growth is only as good as the chemistry it assumes. We shall limit our model to equations 3-5 as the three major reactions. Other reactions could possibly be important[25,26] but they are not the subject of study here. Further, we shall ignore the substitution effect reported on the diamine (equation 4), as the major objective of this study is to report on the importance of the third or the etherification reaction (equation 5), on the network models.

$$\text{(3)}$$

primary amine-epoxy reaction: STEPWISE

$$\text{(4)}$$
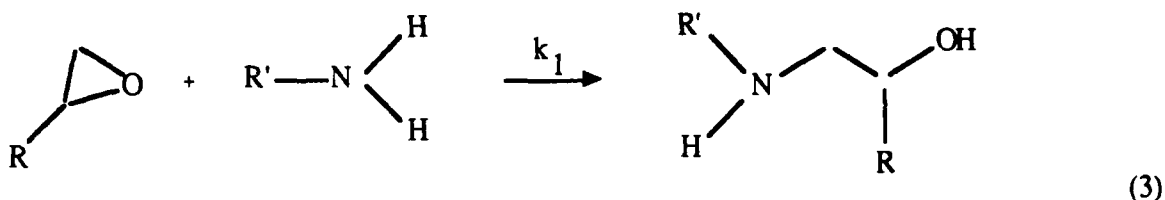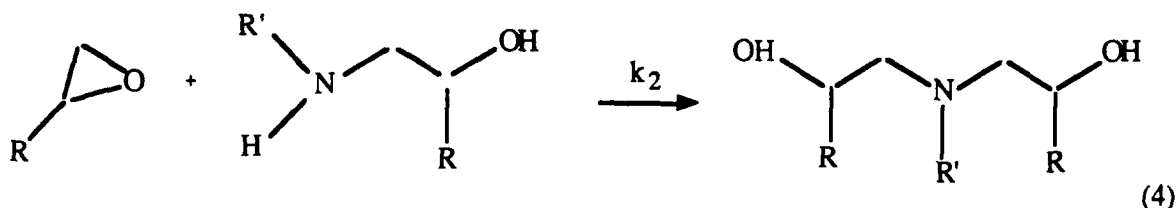
secondary amine-epoxy reaction: STEPWISE (substitution effect on the amine is observed; it will be ignored in this study)

$$\text{(5)}$$

epoxy hydroxyl-epoxy or etherification reaction: "LIVING" ANIONIC

For a comprehensive study of the epoxy chemistry the reader is referred to a review paper by Rozenberg[16]. On the importance of the third reaction, many workers have

reported on epoxy-phenol systems. Here the phenol hydroxyl acts as the initiator for the propogation step between the epoxy hydroxyl and the epoxy. Alvey[27] found (model compounds diglycidyl ether of Bisphenol A and Bisphenol A) that even though the etherification rate became slower with progressive disappearrance of epoxies, it was responsible for gelation in an otherwise linear system. Zukas, Dunn and Gilbert[28] reported etherification as an important reaction even in the case of excess amines (model compounds methoxyglycidyl ether of Bisphenol A and 4,4-aminodiphenyl sulfone). Etherification rate can be promoted by selective catalysts and temperature[29,30]. The phenol-epoxy system has also been studied by Bantle and Burchard[23,24]. They report good agreement with experimental results, even though they ignore the chainwise mechanism in their model.

For most amine-epoxy systems the etherification reaction is considerably slower than the amine-epoxy reaction. Kumar and Gupta[22] have suggested a ratio of around 100 for k_1/k_3 to explain experimental data. This might render some of the previous approximate models[18-20] in good agreement with experimental studies. However, situations can arise in amine-epoxy and similair chemistries where such approximations are poor. One such case is that of excess of epoxies in the initial stoichiometric recipe. Our working premise shall assume reactions 3-5 as the most important reactions, without limiting itself to any relative importance among them.

THE MODELS:

The concept of superspecies[9] can be successfully used to demonstrate the modelling procedure for this chemistry. Superspecies are defined as the minimum number of distinct units in the system, whose combination to yield the network can be statistically considered random. The superspecies must be build kinetically. Non-idealities arising from the failure of the assumptions of the classical Flory-Stockamyer theory to hold, can be tackled by defining an appropriate set of superspecies. For "living" anionic systems the entire chain length distribution constitutes the set of superspecies. Once the distribution of
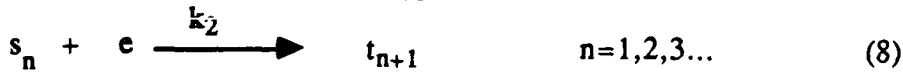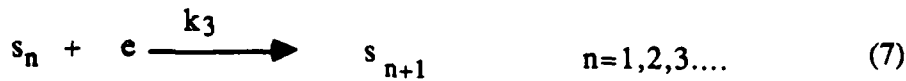
the chains grown starting from an initiator, is solved from the kinetic equations, the statistical models can be used to combine these chains together to form the network. Consider a comparison between the two models we wish to discuss from this perspective.

A. COMBINED MODEL: Our treatment shall use the model first presented by Bokare and Gandhi[21]. This model is exact and overcomes the approximations made in some later studies[17-20]. The complete set of superspecies can be identified by considering the diamine as an initiator. There are two kinds of chains that are grown anionically, depending on the state of reactivity of the amine, those emanating from a secondary amine (Fig 1a) and those from a tertiary amine (Fig 1b). These combined with the unreacted epoxy and unreacted amine constitute the complete set of superspecies.

1) unreacted epoxy (e)

2) unreacted amine (p)

3) secondary amine s_n, with n epoxies attached on the side chain (Fig 1a)

4) tertiary amine t_n, with n epoxies attached on the side chain (Fig 1b)

(paste Fig 1)

The upper limit on n, n_{max}, measured experimentally is an indication of the relative importance of etherification rate. Etherification rate k_3 is zero if $n_{max}=1$ for secondary amine and $n_{max}=2$ for tertiary amine. In the combined model no upper limit is imposed on n_{max}. Having identified the superspecies, we follow the procedure outlined above. We first obtain the concentration profile of the superspecies and then combine them statistically.

For complete detail of the model and its mathematics we refer the reader to the original paper[21]. For sake of completness and since we shall be using the same combined Bokare and Gandhi model for predicting the post-gel properties we briefly reproduce the mathematics here. The reaction equations in terms of the above based abbreviations for the superspecies are:

$$p + e \xrightarrow{\ k_1\ } s_1 \tag{6}$$

$$s_n + e \xrightarrow{\ k_3\ } s_{n+1} \qquad n=1,2,3.... \tag{7}$$

$$s_n + e \xrightarrow{\ k_2\ } t_{n+1} \qquad n=1,2,3... \tag{8}$$

$$t_n + e \xrightarrow{\ k_3\ } t_{n+1} \qquad n=2,3,4... \tag{9}$$

The kinetic equations for the growth of these superspecies are:

$$-\frac{dp}{d\theta} = 2k_1 ep \tag{10}$$

$$-\frac{ds_n}{d\theta} = k_3 e(s_n - s_{n-1}) + k_2 es_n \qquad n \geq 1 \tag{11}$$

$$-\frac{dt_n}{d\theta} = 2k_3 e(t_n - t_{n-1}) - k_2 es_{n-1} \qquad n \geq 2 \tag{12}$$

where t_1 is defined to be zero and θ is the time variable.

To solve this set of infinite differential equations we define probability generating functions:

$$s = \sum_{n=1}^{\infty} z^n s_n \qquad \text{and} \qquad t = \sum_{n=1}^{\infty} z^n t_n \tag{13a \& b}$$

Reducing equations 2 and 3 in terms of s and t as a function of p we obtain:

$$\frac{ds}{dp} = \frac{K_A}{K_O} \frac{s}{p} \left[(1+K_O) - z\right] - z \tag{14}$$

$$\frac{dt}{dp} = 2\frac{K_A}{K_O} \frac{t}{p} (1-z) - K_A \frac{s}{p} z \tag{15}$$

where $K_A = k_2/2k_1$ and $K_O = k_2/k_3$

In our calculations we set $k_1 = k_2$ therefore $K_A = 1/2$ and vary K_O. These equations can be solved analytically to obtain s and t in closed forms. (Equation 20 & 21) Higher derivatives can be used to obtain Σns_n, Σnt_n, $\Sigma n^2 s_n$ and $\Sigma n^2 t_n$.

$$\sum_{n=1}^{\infty} n s_n = \frac{\partial s}{\partial \ln z}\Big]_{z=1} \qquad \sum_{n=1}^{\infty} n t_n = \frac{\partial t}{\partial \ln z}\Big]_{z=1}$$

$$\sum_{n=1}^{\infty} n^2 s_n = \frac{\partial^2 s}{\partial (\ln z)^2}\Big]_{z=1} \qquad \sum_{n=1}^{\infty} n^2 t_n = \frac{\partial^2 t}{\partial (\ln z)^2}\Big]_{z=1} \qquad (16a\text{-}d)$$

These higher derivatives become increasingly tedious to compute and the reader who needs them is referred to the original paper [21]. The formulae we need are reproduced in Appendix A.

We now use the recursive technique[3] to predict the network structure and properties. Looking in and looking out of a randomly chosen epoxy, we write the expectation value of the weight attached to it (see Fig 1). The functionality of the epoxy monomer is g, therefore, the weight looking in a randomly chosen epoxy is the molecular weight of the epoxy and the weight looking out of the other (g-1) epoxies.

$$E(W_e^{in}) = M_e + (g\text{-}1)E(W_e^{out}) \qquad (17)$$

When looking out of an epoxy, it can either be an epoxy attached to a secondary or to a tertiary amine or it could be unreacted:

$$E(W_e^{out}) = \sum_{n=1}^{\infty} \frac{n s_n}{e_o}\left\{(n\text{-}1)E(W_e^{in}) + E(W_a^{in})\right\} + \sum_{n=1}^{\infty} \frac{n t_n}{e_o}\left\{(n\text{-}1)E(W_e^{in}) + E(W_a^{in})\right\}$$

$$(18)$$

The subscripts "a" and "e" stand for amine and epoxy respectively, e_o are the number of initial epoxy monomers. The first term covers the possibility of the epoxy being any of the n epoxies attached to a s_n secondary amine and the second term where it is any of the n epoxies attached to a t_n tertiary amine. If the epoxy is unreacted then there is no weight attached looking out of it.

Similarly choosing an amine at random:

$$E(W_a^{in}) = M_a + (f/2-1)E(W_a out) \qquad (19)$$

where the amine monomer has f hydrogens or $f/2$ amine nitrogens, and p_0 are the number of initial amine monomers. Also the expectation weight looking out of an amine is the sum of the three possibilities, it is a secondary amine, a tertiary amine or it is unreacted.

$$E(W_a^{out}) = \sum_{n=1}^{\infty} \frac{s_n}{p_0} nE(W_e^{in}) + \sum_{n=1}^{\infty} \frac{t_n}{p_0} nE(W_e^{in}) \qquad (20)$$

Solving for the expected weight attached to any epoxy and amine chosen at random

$$E(W_a) = (f/2)E(W_a^{out}) + M_a \qquad (21)$$

$$E(W_e) = gE(W_e^{out}) + M_e \qquad (22)$$

Then the average molecular weight of the reacting system at any given conversion is:

$$M_w = \frac{fM_e}{fM_e + 2\rho gM_a} E(W_e) + \frac{2\rho gM_a}{fM_e + 2\rho gM_a} E(W_a) \qquad (23)$$

where $\rho = p_0/e_0$ is the initial recipe ratio, that is, the number of amino groups to the epoxy groups in the initial recipe. M_a and M_e are the molecular weights of the monomers. The condition for the gel point is:

$$1 = \eta \equiv \rho\,(g-1)\left[(f/2-1)\left\{ \frac{\sum_{n=1}^{\infty}(ns_n+nt_n)}{\rho e_0} \right\}^2 + \left\{ \frac{\sum_{n=1}^{\infty}(n^2s_n+n^2t_n)}{\rho e_0} \right\} - \left\{ \frac{\sum_{n=1}^{\infty}(ns_n+nt_n)}{\rho e_0} \right\} \right]$$

$$(24)$$

B. RANDOM MODEL: We call any model that fails to recognize the chainwise nature of the etherification reaction, random. In these models[18-20] the distinct units that compose the network are identified (Fig 2) and kinetic equations solved for their concentration profile. Then the statistical arguments are employed to develop the network. The units chosen thus, are not sensitive to the operative growth mechanism, and therefore they are not random in their statistics. It would be incorrect to call them superspecies, a name reserved for units that are chemically random in their statistics. For bifunctional diamines and epoxies eight structures can be isolated as these units (Fig 2). We label such models random, because they would have the correct units as the superspecies if the mode of reaction was stepwise only.

(paste Fig 2)

The details of the modelling strategy for such models has also be reported in the literature[18-20]. Again for the sake of completness we have derived the model kinetics and statistics based on the units in Fig 2, in Appendix B. We shall use the results derived there to compare with the predictions of the combined model.

Among the past work in this area, Riccardi and Williams (along with Dusek)[30], have recognized the approximate nature of their earlier model[18] and the concept of fragments has been used to highlight this difference.

C. POSTGEL CALCULATIONS: Having concluded that the random model is an approximation to the chemistry (equations 3-5), we shall extend only the combined or the Bokare and Gandhi model to predict the post-gel properties of the amine-epoxy systems. For the postgel calculations the set of superspecies remains the same as in the pregel stage and the same kinetic equations are used. The statistics is now defined in terms of expectation values of discovering a finite weight attached to a molecule, when a unit on it, is chosen at random.

We pick an epoxy at random and calculate the probability that the weight attached to the epoxy looking out and looking in is finite [31].

$$P(F_e^{in}) = [P(F_e^{out})]^{(g-1)} \tag{24}$$

Looking in, the finite probability implies that the weight attached looking out of the other 'g-1) epoxies on the monomer is finite. Looking out of the randomly chosen epoxy the following possibilities exist:

1) It is attached to a secondary amine s_n with the probability : $p = ns_n/e_0$ (Fig 1a group E)

2) It is attached to a tertiary amine t_n with the probability : $p = nt_n/e_0$ (Fig 1b group E)

3) It is an unreacted epoxy with the probability : $p = \{1-\Sigma(ns_n+nt_n)\}/e_0 = e/e_0$

If the epoxy chosen at random is reacted, and it is a part of a moelcule with finite weight, the weight looking into all the units attached to it must be finite. If the epoxy is unreacted the probability that the weight looking out of it, is finite, is unity.

$$P(F_e^{out}) = \sum_{n=1}^{\infty} \frac{ns_n}{e_0} \left[\{P(E_e^{in})\}^{n-1} * P(F_a^{in}) \right] + \sum_{n=1}^{\infty} \frac{nt_n}{e_0} \left[\{P(E_e^{in})\}^{n-1} * P(F_a^{in}) \right]$$

$$+ \left(1- \sum_{n=1}^{\infty} \frac{ns_n + nt_n}{e_0} \right)$$

$$\tag{25}$$

Similarly choosing an amine at random, the probability that the weight attachedto it, looking in, is finite, if the weight attached looking out of the other (f/2-1) units on the monomer, is finite

$$P(F_a^{in}) = \{P(F_a^{out})\}^{(f/2-1)} \tag{26}$$

Looking out of a randomly chosen amine we again distinguish between :

1) secondary amine s_n ;probability $p = s_n/p_0$ (Fig 2a group A)

2) tertiary amine t_n ; probability $p = t_n/p_0$ (Fig 2b group A)

3) unreacted amine p ; probability $p = p/p_0 = 1-\{\Sigma(s_n+t_n)/p_0\}$

Then:

$$P(F_a^{out}) = \sum_{n=1}^{\infty} \frac{s_n}{p_o} \left\{ P(F_e^{in}) \right\}^n + \sum_{n=1}^{\infty} \frac{t_n}{p_o} \left\{ P(F_e^{in}) \right\}^n + \left\{ 1 - \left(\sum_{n=1}^{\infty} \frac{s_n + t_n}{p_o} \right) \right\}$$

(27)

In the first term, when the amine chosen happens to be a secondary amine s_n, the weight looking into the n epoxies on that chain must be finite and similarly if the amine happens to be a tertiary amine. Finally the last term reflects the fact that if the amine were unreacted the probability of finite weight attached to it, looking out, is unity.

These are a set of four non-linear equations 24-27 in four variables, $P(F_e^{in})$, $P(F_e^{out})$, $P(F_a^{in})$, $P(F_a^{out})$ for each n. We again use probability or moment generating functions to simplify these to four equations for all n.

$$s = \sum_{n=1}^{\infty} z^n s_n \qquad\qquad t = \sum_{n=1}^{\infty} z^n t_n$$

$$\frac{ds}{dz} = \sum_{n=1}^{\infty} n\, z^{n-1} s_n \qquad\qquad \frac{dt}{dz} = \sum_{n=1}^{\infty} n\, z^{n-1} t_n \qquad (28\ a\text{-}d)$$

and we set $z = E(F_e^{in})$ in 28 a-d.

We have already obtained s and t as a function of z from our kinetic analysis in the pregel stage

$$\frac{s}{e_o} = \frac{z\rho}{\lambda - 1} \left[\frac{p}{p_o} - \left(\frac{p}{p_o} \right)^{\lambda} \right]$$

(29)

$$\frac{t}{e_o} = \frac{z^2 K_A \rho}{(\lambda - 1)(1 - \gamma)(\lambda - \gamma)} \left[(1 - \gamma)\left(\frac{p}{p_o} \right)^{\lambda} - (\lambda - \gamma)\left(\frac{p}{p_o} \right) + (\lambda - 1)\left(\frac{p}{p_o} \right)^{\gamma} \right]$$

(30)

where $\lambda = \frac{K_A}{K_O}(1 + K_O z)$ and $\gamma = \frac{2K_A}{K_o}(1 - z)$

Performing the above mentioned steps we are left with four non-linear equations 24-27, in four variables that can be solved numerically to compute the finite weight expectation probabilities. The equations and the numerical method are delineated in Appendix A. We performed the numerical analysis to predict the weight fraction of sol in the post-gel stage. Other properties of the network, e.g. crosslink density can be similarly computed[31-33]. To enable the reader to do these directly we also present the finite expectation values for two interesting cases.

RESULTS

A. PREGEL STAGE: Since we wish to highlight the effect of etherification reaction in this paper we will ignore the substitution effect on the amine groups. There are two important extremes in making these networks, where the concerns we have talked about become dominant.

1) The case where the rate of etherification is faster than the amine-epoxy addition reaction; that is $k_3 > k_1$

2) The case where the network is formed with an excess of epoxies in the initial stoichiometric recipe; i.e. $r = 2p_o/e_o < 1$

Under both these operating conditions the predictions of the two models discussed would be significantly different. There is a paucity of experimental results where networks are produced under either of the above mentioned conditions. There is a commercial epoxy resin using an excess of epoxies (DGEBA) with a secondary amine (diethanonal amine)[34]. We are currently attempting to study the experimental aspects of this chemistry; however, for the purposes of this paper we shall restrict ourselves to the theoretical modelling considerations of such networks.

To highlight the effect of etherification rate on the network structure, in Fig 3 and 4 the weight average molecular weight profile as a function of the epoxy conversion is plotted, for both the models. In Fig 3 the rate of etherification is ten times faster than the

amine-epoxy addition rate. The magnitude of the deviations between the two models is significant. In Fig 4 where the etherification rate is ten times slower, there is still an appreciable difference in the predictions of the two models, but as the relative rate of etherification becomes vanishingly small the predictions of the two models become identical. In both Fig 3 and 4, $k_1=k_2$ and the initial stoichiometry was balanced, that is, $2p_0=e_0$ or $\rho=1/2$. Further these and other results presented here are for bifunctional epoxy ($g=2$) and bifunctional amine ($f/2=2$).

In Table 1, the gel point predictions (as the conversion of the hydrogen in the network at the gel point) are presented for the two models. As long as $k_3/k_1<1$ the differences between the two models are small, but as the rate of etherification becomes significant the need for employing the correct combined model is obvious. In Fig 5 the same data is presented in a graphical form for interpolation purposes.

To delineate the effect of imbalanced stoichiometry on the network structure in Table 2 and 3, the gel point is presented for different stoichiometric ratios r; r is the number of hydrogens to the number of epoxies i.e. $2p_0/e_0$. In Table 2 the rate of etherification is ten times slower whereas in Table 3 it is ten times faster. When k_3/k_1 is less than unity and r is greater than unity the predictions of the two models are within a few percent of each other. In this limit the epoxy-hydroxyl reaction is almost absent and the predictions of the two models should indeed be same. Further intuitively one would expect the combined model to predict a faster gel point and a sharper growth profile as it faithfully models the chainwise reaction. This too is observed.

As an interesting situation consider the case where the number of epoxies are four times the number of hydrogens in the initial recipe. Further assume that the amine-epoxy system is such that the rate of etherification is ten times slower than the rate of amine-epoxy addition. Then Table 2 suggests that the random model would predict that even at complete hydrogen conversion the system does not gel, whereas the combined model predicts a gel point at 92% hydrogen conversion and 27% epoxy conversion. Under situations like this where the rate of etherification is a order of magnitute less than the main reaction, a random model would still be inadequate as it ignores the operative growth

chemistry. Any random model irrespective of the statistics it employs, either combinatorial methods[1], probability generation functions [2]or the recursive approach[3] assumes equal accessibility of all reactable sites. In essence it makes the following three assumptions:

1) all units are equally accessible to the reaction

2) all units combine with equal randomness irrespective of the state of the neighoring groups or the size of the growing molecule

3) all intramolecular reactions in finite species are ignored, ie no loop formation.

In chainwise addition reaction where the reaction is conditional upon initiation, chains do not grow randomly and long range correlations are important. These correlations change the nature of the statistical distribution of linear chains to a Poisson distribution[13], assuming all initiations occurred at the same time. Assumptions one and three are unavoidable at present, but two is unrealistic and unneccessary. It is for this reason that the need to understand the chemistry of the network growth before proceeding to build an appropiate model for it is important.

B. POSTGEL STAGE: In order to predict the various network structural properties in the post gel stage, the probabilities of the molecule being finite ,looking out of a randomly chosen amine or epoxy are needed. In Fig 6 we plot these finite weight probabilities looking out of an epoxy for the cases where the rate of etherification is ten times faster and ten times slower. In Fig 7 we plot the same probabilities for the amines. In the case of faster etherification rate when the epoxy conversion is 99% the amine conversion is only 46%, though they where in stoichiometric balance initially and the finite probability looking out an amine is only 47%. Such systems would show an excess of unreacted epoxy even when the amines are driven to exhaustion. Finally in Fig 8 the effect of stoichiometric ratio on the weight fraction solubles during the postgel stage is depicted. The weight fraction solubles are given by:

$$w_s = w_a P(F_a^{out})^{f/2} + w_e P(F_e^{out})^g \qquad (31)$$

where $w_a = 2\rho g M_a/(2\rho g M_a + f M_e)$ is the weight fraction of the amines in the network and $w_e = f M_e/(2\rho g M_a + f M_e)$ is the weight fraction of the epoxies in the network. Again the effect of imbalance is to leave an excess of epoxies unreacted that are slowly driven to exhaustion.

LIMITING CASES OF THE COMBINED MODEL

Since it contains both growth mechanisms, the combined model can be used to predict the network structure, in either of the two operating extremes. If the network chemistry is purely random we set $k_3 = 0$. If the reaction growth is entirely anionic, the amine-epoxy reaction can be considered as the initiation step and the epoxy-epoxy reaction as the propogation step. Further, the combined model overcomes two assumptions often made in anionic growth models[5]:

1) the initiation step is instantaneous.

2) the number of initiators are few compared to the monomers.

In the combined model any number of initiators can be used. Though the equations presented here are limited to bifunctionally paired initiators they can be easily extended to the general case, as it only requires modifying the recursive analysis. The combined model is however, limited to cases similar to "living" anionic polymerization since it contains no termination steps.

SUMMARY

We have compared two available models in the literature for treating polymer networks that produce a secondary site which reacts through a different growth chemistry with specific application to amine-epoxy systems. We have explained why a model that operates entirely in the step growth paradigm is erroneous and that the exact model must consider the chainwise nature of etherification reaction kinetically. We have cast these differences in the general framework of superspecies. We have shown that the difference in the predictions of the two models can be substantial and highlighted such situations. Further, we have extended the combined model to predict the network properties in the

postgel stage of the amine-epoxy systems.

ACKNOWLEDGEMENT

APPENDIX A (POSTGEL CALCULATIONS)

First we give equations for the first partial derivatives of the probability generating functions **4a** &b.

$$\sum_{n=1}^{\infty} \frac{ns_n + nt_n}{e_o} \quad = \quad \frac{1}{e_o} \frac{\partial (s+t)}{\partial \ln z} \Bigg]_{z=1}$$

$$= \rho \left[\frac{1}{(K_A - 1)} \left\{ \frac{P}{P_O}\left(\frac{K_A}{K_O(K_A-1)} + 1 \right) - \left(\frac{P}{P_O}\right)^{K_A}\left(1 + \frac{K_A}{K_O(K_A - 1)} - \frac{K_A}{K_O} \ln \frac{p}{p_o} \right) \right\} \right]$$

$$+ \frac{\rho}{K_A - 1} \left[\frac{K_A}{K_O}\left(\frac{P}{P_O}\right)^{K_A}\left(2 - \ln\frac{p}{p_o} \right) - \frac{K_A}{K_O}\left(1 + \frac{P}{P_O} \right) - \frac{2K_A}{K_O}(K_A - 1)\ln\frac{p}{p_o} \right]$$

$$+ \frac{\rho}{K_A - 1} \left[\left(\frac{p}{p_o}\right)^{K_A} - K_A\frac{P}{P_O} + K_A - 1 \right]\left[2 + \frac{1}{K_O(K_A - 1)} - \frac{K_A 2}{K_O} \right]$$

$$\tag{A1}$$

and

$$\frac{1}{\rho}\left[\frac{\displaystyle\sum_{n=1}^{\infty} \{ns_n + nt_n\}}{e_o} \right] P(F_e^{in})^{n-1} = \frac{1}{\rho} \frac{\partial}{\partial z} (s + t) \Bigg]_{z=P(F_e^{in})}$$

$$= \frac{z}{(w1 - 1)}\left[\frac{1}{z} + \frac{K_A}{K_O(w1 - 1)} \right]\left[\frac{p}{p_o} - \left(\frac{p}{p_o}\right)^{w1} \right] + \frac{1}{(w1 - 1)}\left[\frac{K_A}{K_O} * z * \ln \frac{p}{p_o} * \left(\frac{p}{p_o}\right)^{w1} \right]$$

$$+ w3\frac{K_A}{K_O}\left[2\left(\frac{p}{p_o}\right)^{w1} - \frac{p}{p_o} - \left(\frac{p}{p_o}\right)^{w2} - \frac{K_A}{K_O} \ln\frac{p}{p_o}\left\{ 2(w1-1)\left(\frac{p}{p_o}\right)^{w2} + \left(\frac{p}{p_o}\right)^{w1}(1-w2) \right\} \right]$$

$$+ w3 \left[(1-w2)\left(\frac{p}{p_0}\right)^{w1} - (w1 - w2)\frac{p}{p_0} + (w1-1)\left(\frac{p}{p_0}\right)^{w2} \right] \left[\frac{2}{z} + \frac{K_A}{K_O(w1-1)} - \frac{2K_A}{K_O(1-w2)} - \frac{K_A}{K_O(w1-w2)} \right]$$

$$(A2)$$

where

$$w1 = \frac{K_A}{K_O}(1 - z + K_O)$$

$$w2 = \frac{2K_A}{K_O}(1-z)$$

$$w3 = \frac{z^2 K_A}{(w1-1)(1-w2)(w1-w2)}$$

and

$$z = P(W_e^{in})$$

The solution to equations 24-27 is obtained by assuming a value of $P(F_e^{in})$ which is necessarily between zero and one. Then equation 27 can be solved by using equations A1 and A2 with $z=1$ and $z=P(F_e^{in})$ for the last and the first two terms respectively. 26 can be solved using 27. To solve 25 the first partial derivatives of the probability generating functions are needed with $z=1$ and $z=P(F_e^{in})^{n-1}$ which are given by equations A1 and A2. Having solved 25, 24 can be solved to obtain $P(F_e^{in})$. This value is compared with the assumed root and the analysis repeated till desired tolerance is achieved. This technique is not the most robust mathematically but suffices in this case.

APPENDIX B (RANDOM MODEL)

Calculations for the purely Markovian or random model:

Notation:

$[N_1]$ = # of secondary amines

$[N_{1,2}]$ = # of tertiary amines

$[Ep_1]$ = # of epoxies reacted with amine only

$[Ep_{1,2}]$= # of epoxies reacted with amine and epoxy

$[Ep_{2,2}]$= # of epoxies reacted with epoxy and epoxy

$[Ep_2]$ = # of epoxies reacted with one epoxy

$[N_o]$ = # of unreacted amines at any instant

$[N_T]$ = # of total amines

$[Ep_o]$ = # of unreacted epoxies at any instant

$[Ep_T]$ = # of total epoxies

f = # of hydrogens on the amine monomer

g = functionality of the epoxy monomer

ρ = $[N_T]/[Ep_T]$ the initial recipe ratio

x = $[N_o]/[N_T]$

α = $k_3/2k_1$

REACTIONS

$$N_o + Ep_o \xrightarrow{k_1} N_1 + Ep_1$$

$$N_1 + Ep_o \xrightarrow{k_2} N_{1,2} + Ep_1$$

$$Ep_1 + Ep_o \xrightarrow{k_3} Ep_{1,2} + Ep_2$$

$$Ep_2 + Ep_o \xrightarrow{k_3} Ep_{2,2} + Ep_2$$
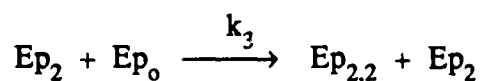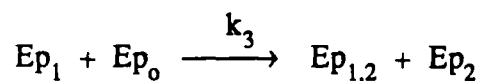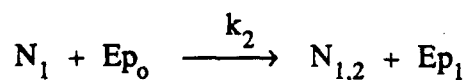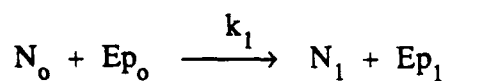
Assuming $k_1=k_2$ and defining $\alpha = k_3/2k_1$ the differential equations for the above reactions can be solved in terms of x the concentration of unreacted amines in the network.

The differential equations for this growth kinetics are:

$$-\frac{d[N_o]}{dt} = 2k_1[N_o][Ep_o]$$

$$-\frac{d[N_1]}{dt} = -2k_1[N_o][Ep_o] + k_1[N_1][Ep_o]$$

$$-\frac{d[N_{1,2}]}{dt} = -k_1[N_1][Ep_0]$$

$$-\frac{d[Ep_1]}{dt} = k_3[Ep_1][Ep_o] - 2k_1[N_o][Ep_o] - k_1[N_1][Ep_o]$$

$$-\frac{d[Ep_{1,2}]}{dt} = -k_3[Ep_1][Ep_o]$$

$$-\frac{d[Ep_2]}{dt} = -k_3[Ep_1][Ep_o]$$

$$-\frac{d[Ep_{2,2}]}{dt} = -k_3[Ep_2][Ep_o]$$

$$-\frac{d[Ep_o]}{dt} = 2k_1[N_o][Ep_o] + k_1[N_1][Ep_o] + k_3[Ep_1][Ep_o] + k_3[Ep_2][Ep_o]$$

(B1-8)

Two cases in terms of α emerge:

    1) $\alpha \neq .5$

then

$$p_I = \frac{N_1}{N_T} = -2x + 2\sqrt{x}$$

$$p_{II} = \frac{N_{1,2}}{N_T} = x - 2\sqrt{x} + 1$$

$$p_1 = \frac{Ep_1}{E_T} = \rho\left[\frac{2}{1-2\alpha}(x^\alpha - \sqrt{x})\right]$$

$$p_2 = \frac{Ep_2}{E_T} = \rho\left[\frac{2\alpha}{1-2\alpha}(2\sqrt{x} - \frac{x^\alpha}{\alpha}) + 2\right]$$

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$$p_{1,2} = \frac{Ep_{1,2}}{E_T} = p_2$$

$$p_{2,2} = \frac{Ep_{2,2}}{E_T} = \rho \left[\frac{2\alpha^2}{1-2\alpha} \left(\frac{x^\alpha}{\alpha^2} - 4\sqrt{x} \right) - 2\alpha \ln x - 2(1+2\alpha) \right]$$

$$p_o = \frac{E_o}{E_T} = 1 - (p_1 + p_2 + p_{1,2} + p_{2,2}) = 1 - \rho \left[2(1-2\alpha) + 2\alpha \ln x + (2-4\alpha)\sqrt{x} \right]$$

(B9-15)

2) when $\alpha = .5$

$$p_I = -2x + 2\sqrt{x}$$

$$p_{II} = x - 2\sqrt{x} + 1$$

$$p_1 = -\rho(\sqrt{x} \ln x)$$

$$p_2 = \rho(\sqrt{x} \ln x - 2\sqrt{x} + 2)$$

$$p_{1,2} = \rho(\sqrt{x}(\ln x - 2) + 2)$$

$$p_{2,2} = \rho(-\ln x + 4\sqrt{x} - \sqrt{x} \ln x - 4)$$

$$p_0 = 1 + \rho \ln x$$

(B16-22)

Armed with these probabilities one uses statistical arguments to build the network structure. Using the recursive technique[3] the expectation value of weight looking in and out of a randomly chosen epoxy and amine is determined. In order to do that the following probabilities are also needed:

$$p_{1s} = \text{epoxy reacted with secondary amine only} = p_1 \sqrt{x}$$

$$p_{1t} = \text{epoxy reacted with tertiary amine only} = p_1 - p_{1s}$$

$$p_{1,2\,s} = \text{epoxy reacted with epoxy and secondary amine} = p_{1,2} \sqrt{x}$$

$$p_{1,2\,t} = \text{epoxy reacted with epoxy and tertiary amine} = p_{1,2} - p_{1,2} \sqrt{x}$$

(B23-26)

Then

$$E(W_{ep}^{out}) = (p_1 + p_{1,2})\, E(W_{am}^{in}) + (p_{1t} + p_{1,2} + p_{1,2t} + p_2 + 2p_{2,2})\, E(W_{ep}^{in})$$

$$E(W_{ep}^{in}) = M_{ep} + (g-1)\, E(W_{ep}^{out})$$

$$E(W_{am}^{out}) = (p_I + 2p_{II})\, E(W_{ep}^{in})$$

$$E(W_{am}^{in}) = M_{am} + (f/2 - 1)\, E(W_{am}^{out})$$

$$(B27\text{-}30)$$

Solving these and substituting for the molecular weight one gets the following criterion for the gel point:

$$1 = \eta \equiv (g-1)\left[(p_1 + p_{1,2})\,(f/2 - 1)\,(p_I + p_{II}) + (p_{1t} + p_{1,2t} + p_{1,2} + p_2 + 2p_{2,2}) \right]$$

and

$$M_w = \frac{fM_{ep}}{fM_{ep} + 2\rho g M_{am}} E(W_{ep}) + \frac{2\rho g M_{am}}{fM_{ep} + 2\rho g M_{am}} E(W_{am})$$

$$(B31\text{-}32)$$

$$\text{where } E(W_{ep}) = gE(W_{ep}^{out}) + M_{ep} \qquad (B33)$$

$$E(W_{am}) = (f/2)E(W_{am}^{out}) + M_{am} \qquad (B\ 34)$$

$$E(W_{ep}^{out}) = \frac{(p_1+p_{1,2})(M_{am}+(f/2-1)(p_I+p_{II})M_{ep}) + (p_{1t}+p_{1,2t}+p_2+p_{1,2}+2p_{2,2})M_{ep}}{1-\eta} \qquad (B\ 35)$$

$$E(W_{am}^{out}) = (p_I+2p_{II})(M_{ep}+(g-1)E(W_{ep}^{out})) \qquad (B\ 36)$$

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13) To appreciate why the distribution is Poisson, for "living" anionic polymerization in linear systems with instanatenous initiation all occuring at the same time, recall why the distribution must be geometric (most probable) in stepwise systems. If p (number of reacted units / number of total units) is the conversion, the probability that a randomly chosen chain is n units long is equal to the probability that (n-1) units have reacted and one has not ; i.e. $p^{n-1}(1-p)$, which is the geometric distribution. In anionic systems suppose there is only one initiator per chain, then the probability of a chain being initiated is $p = 1/I_0$, where I_0 are the total # of initiators. Each reactive site can choose any of the initiated chains to grow; with an equal probability p. Therefore the probability that a randomly chosen chain is n units long is binomial with parameters n and p, to which the

Poisson is an excellent approximation (For a mathematical understanding of the terms Poisson and geometric distribution refer to any text on probability, e.g. *Introduction to Probability* by Hoel, P.G.; Port, S.C.; Stone, C.J.; Houghton Mifflin Co, Boston, **1971**).

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CAPTIONS FOR FIGURES:

FIG 1a: General structure of a secondary amine s_n

FIG 1b: General structure of a tertiary amine t_n

FIG 2: Smallest statistical units needed in the random model to knit the network fabric

FIG 3: Weight average molecular weight vs epoxy conversion for both the random and combined model; balanced stoichiometry, $r=1$; epoxy functionality $g=2$; amine functionality $f=4$; rate of etherification $k_3=.1k_1$ and $k_1=k_2$.

FIG 4: Weight average molecular wight vs epoxy conversion for both the random and combined model; $r=1$, $f=4$, $g=2$, $k_3=10k_1$ and $k_1=k_2$.

FIG 5: The conversion of hydrogens at the gel point vs the ratio of the rate of etherification k_3 to the primary amine - epoxy reaction rate k_1; $r=1$, $f=4$, $g=2$ and $k_1=k_2$.

FIG 6: The finite probabilities looking out of an epoxy as a function of epoxy conversion for two rate ratios; $r=1$, $f=4$, $g=2$ and $k_1=k_2$.

FIG 7: The finite probabilities looking out of an amine as a function of epoxy conversion for two rate ratios; $r=1$, $f=4$, $g=2$ and $k_1=k_2$.

FIG 8: The weight fraction solubles plotted as a function of epoxy conversion for different stoichiometric ratios r; $k_3=10k_3$, $k_1=k_2$, $f=4$, $g=2$.

the other (f/2-1) amine groups
GROUP A

the other (g-1) epoxy groups
GROUP E
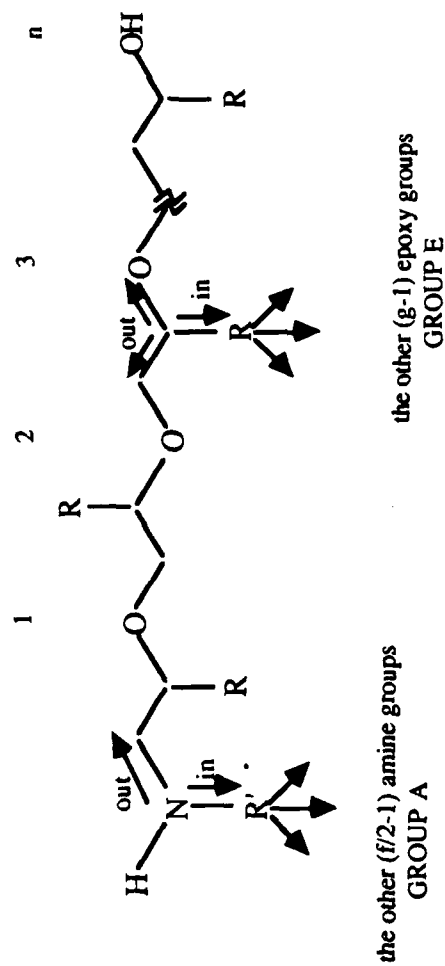
FIG 1a): General structure of a secondary amine group s_n

the other (f/2-1) amine groups
GROUP A

the other (g-1) epoxy groups
GROUP E
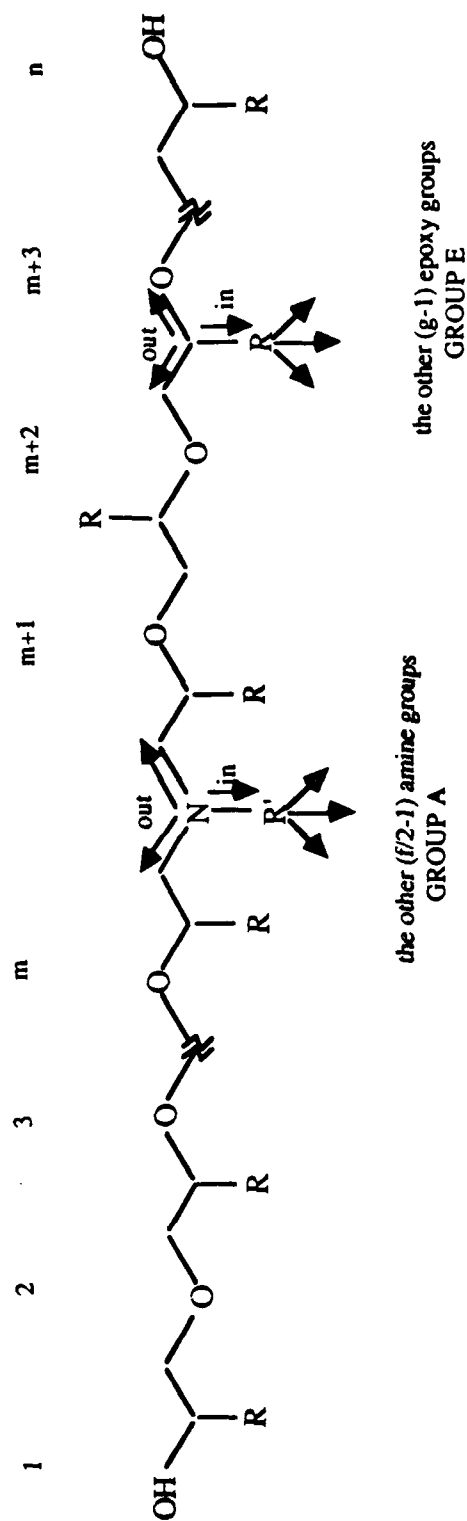
FIG 1b): General structure of a tertiary amine group t_h

1) PRIMARY AMINE [N_0]
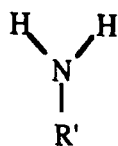
2) SECONDARY AMINE [N_1]
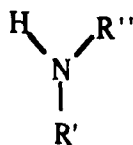
3) TERTIARY AMINE [$N_{1,2}$]
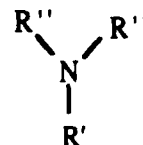
4) UNREACTED EPOXY [Ep_0]
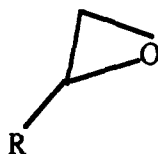
5) EPOXY REACTED WITH AMINE [Ep_1]
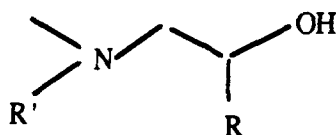
6) EPOXY REACTED WITH EPOXY [Ep_2]
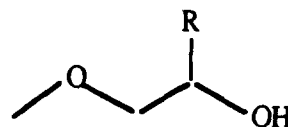
7) EPOXY REACTED WITH AMINE AND EPOXY [$Ep_{1,2}$]
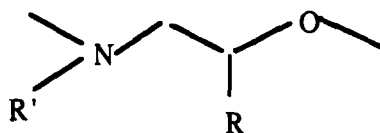
8) EPOXY REACTED WITH EPOXY AND EPOXY [$Ep_{2,2}$]
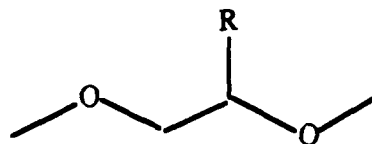
Fig 2: Smallest statistical units needed in the random model to knit the network fabric

FIG 3
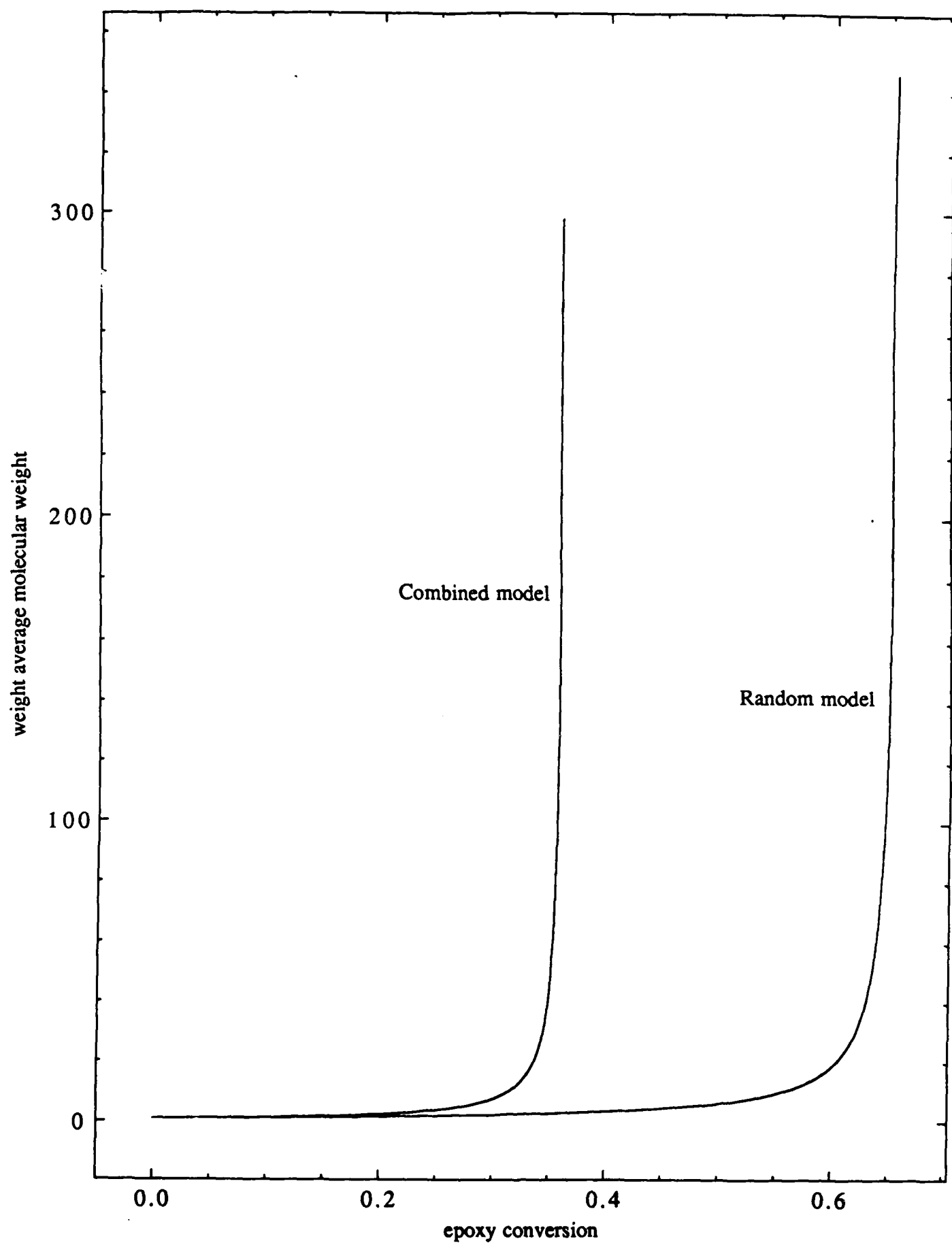
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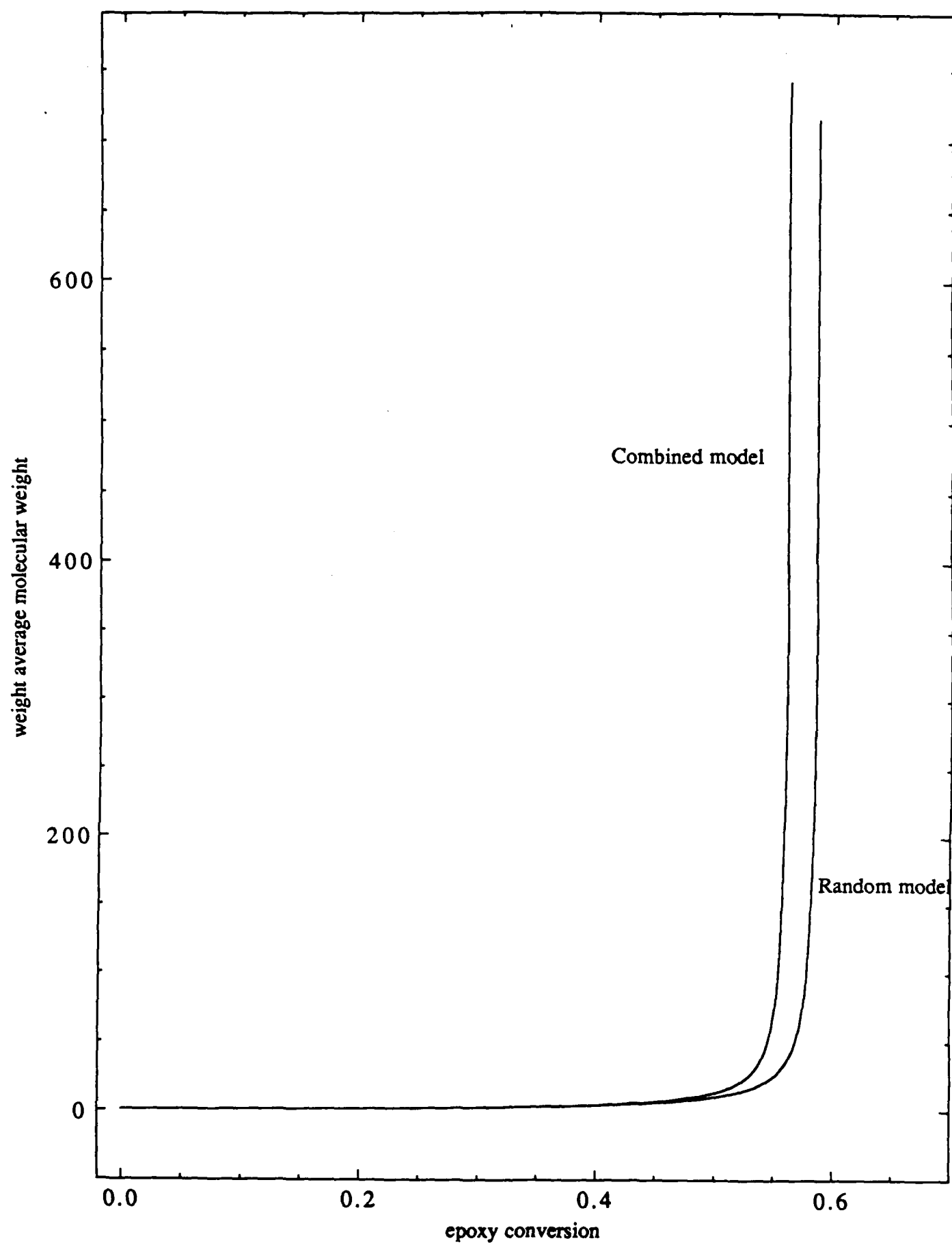
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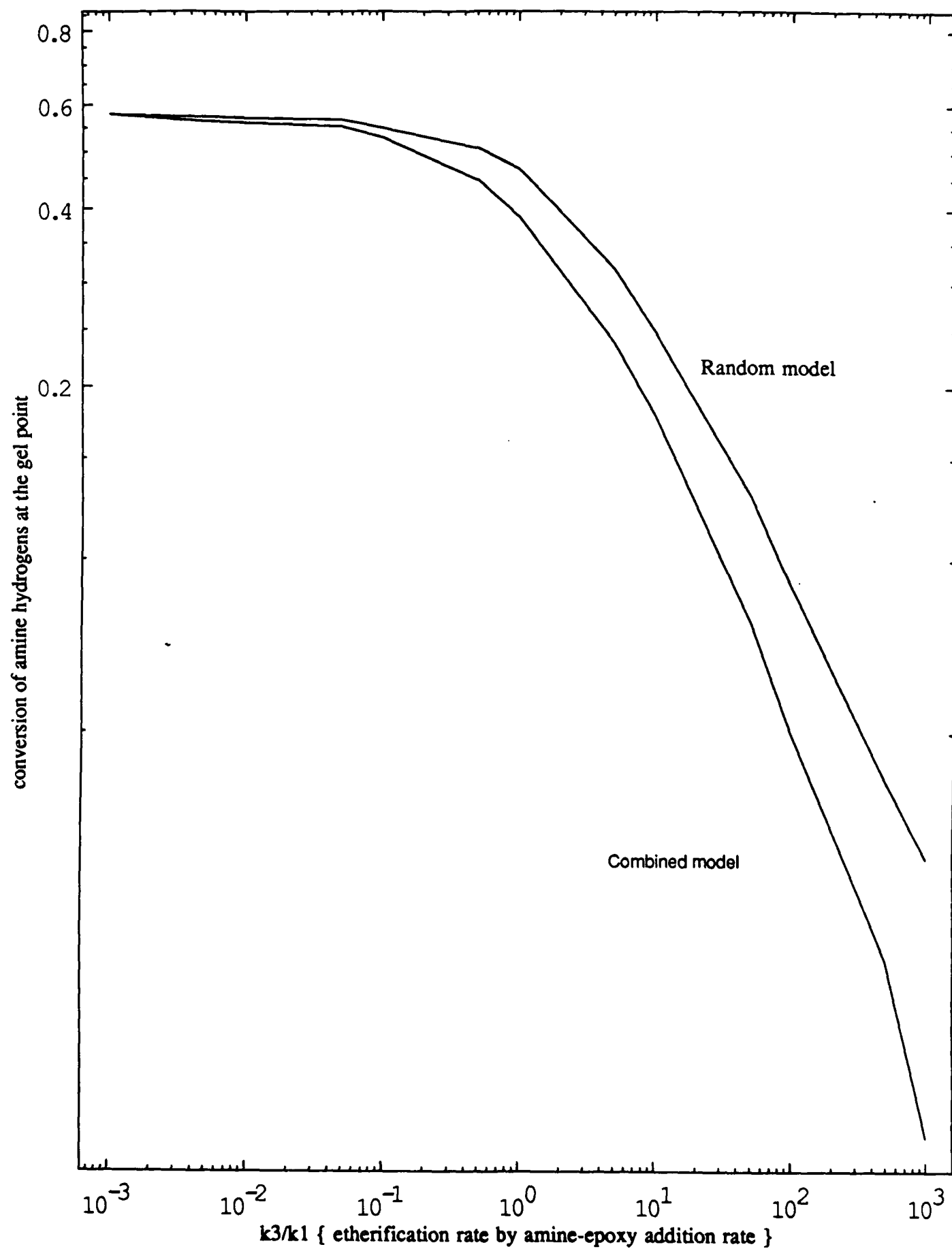
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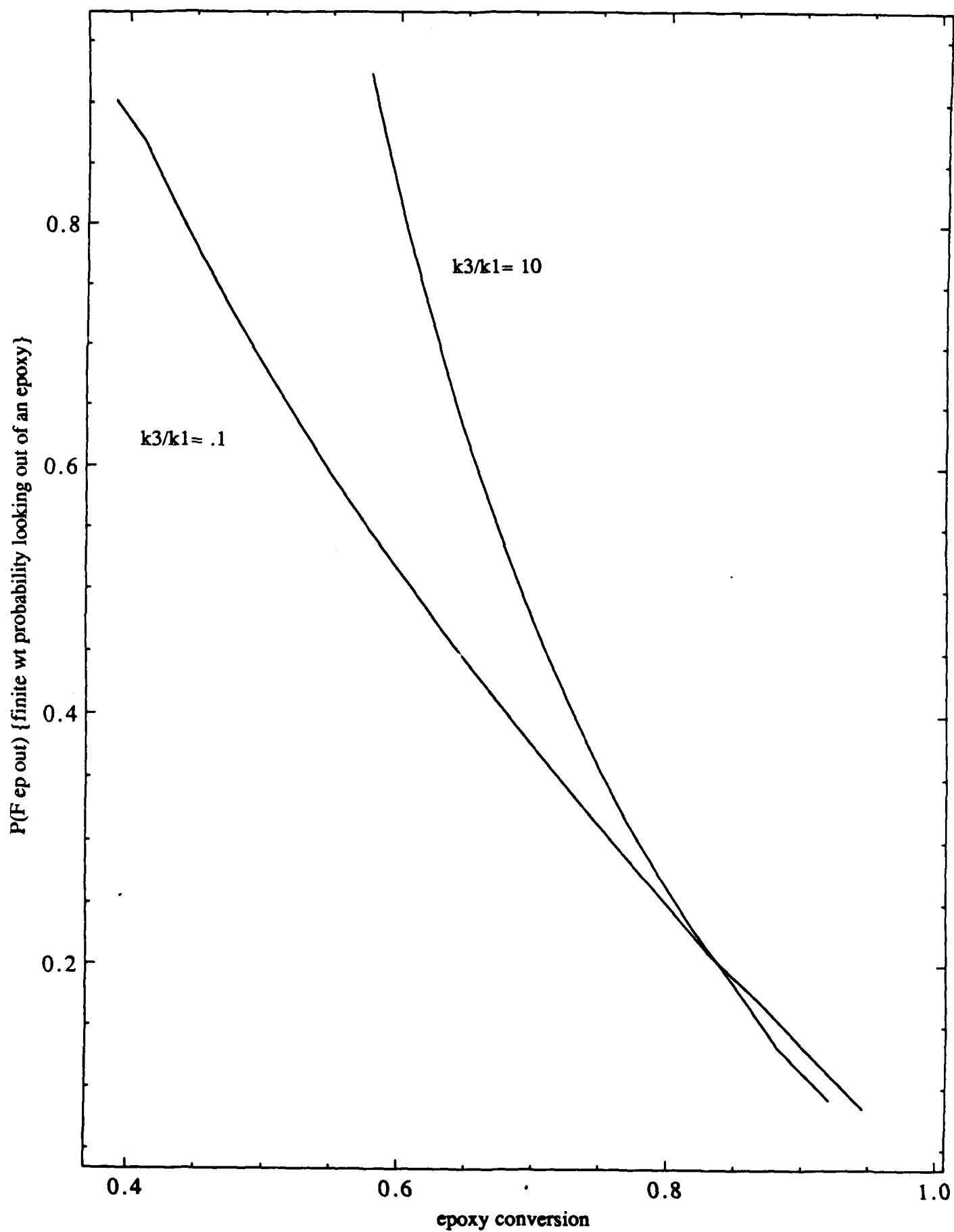
FIG7
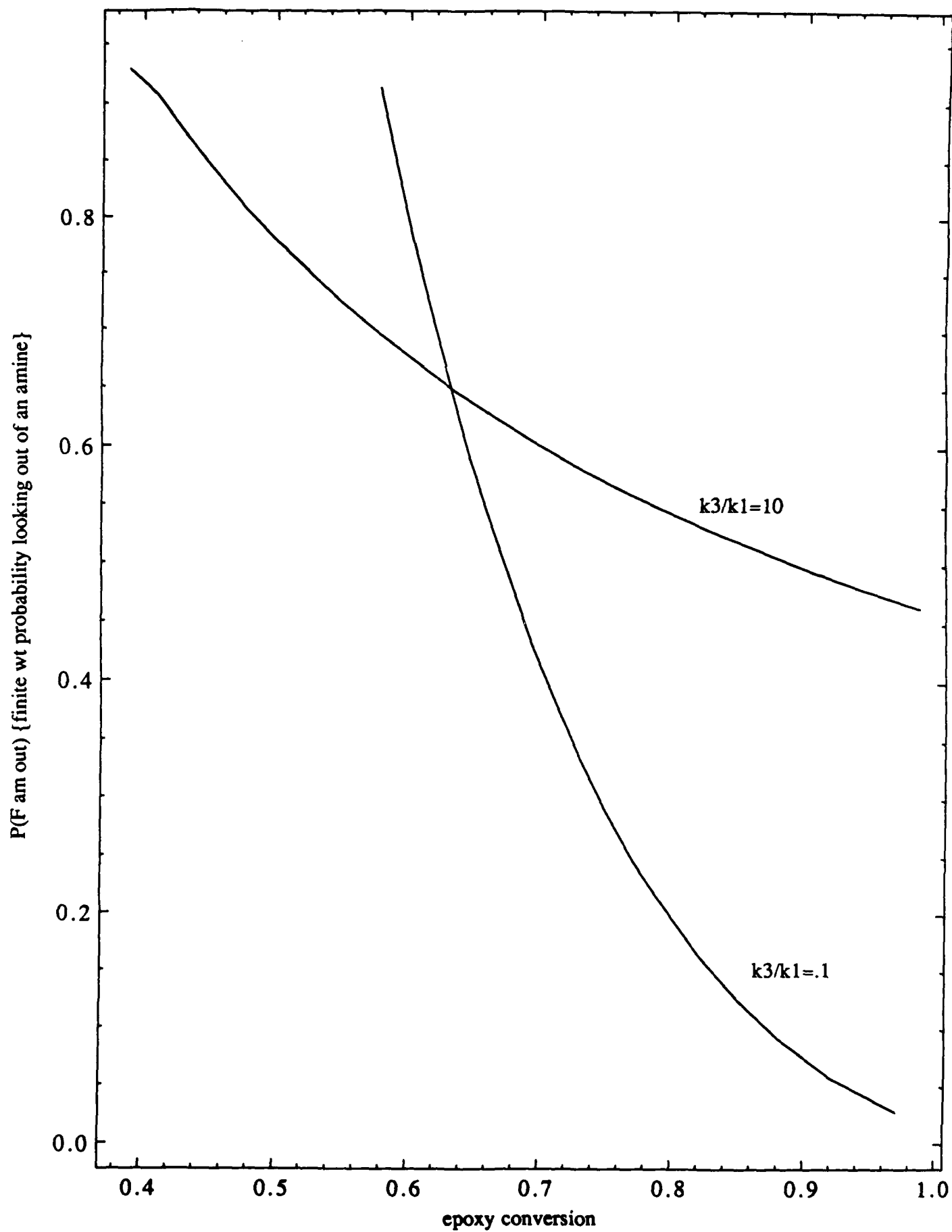
FIG 8
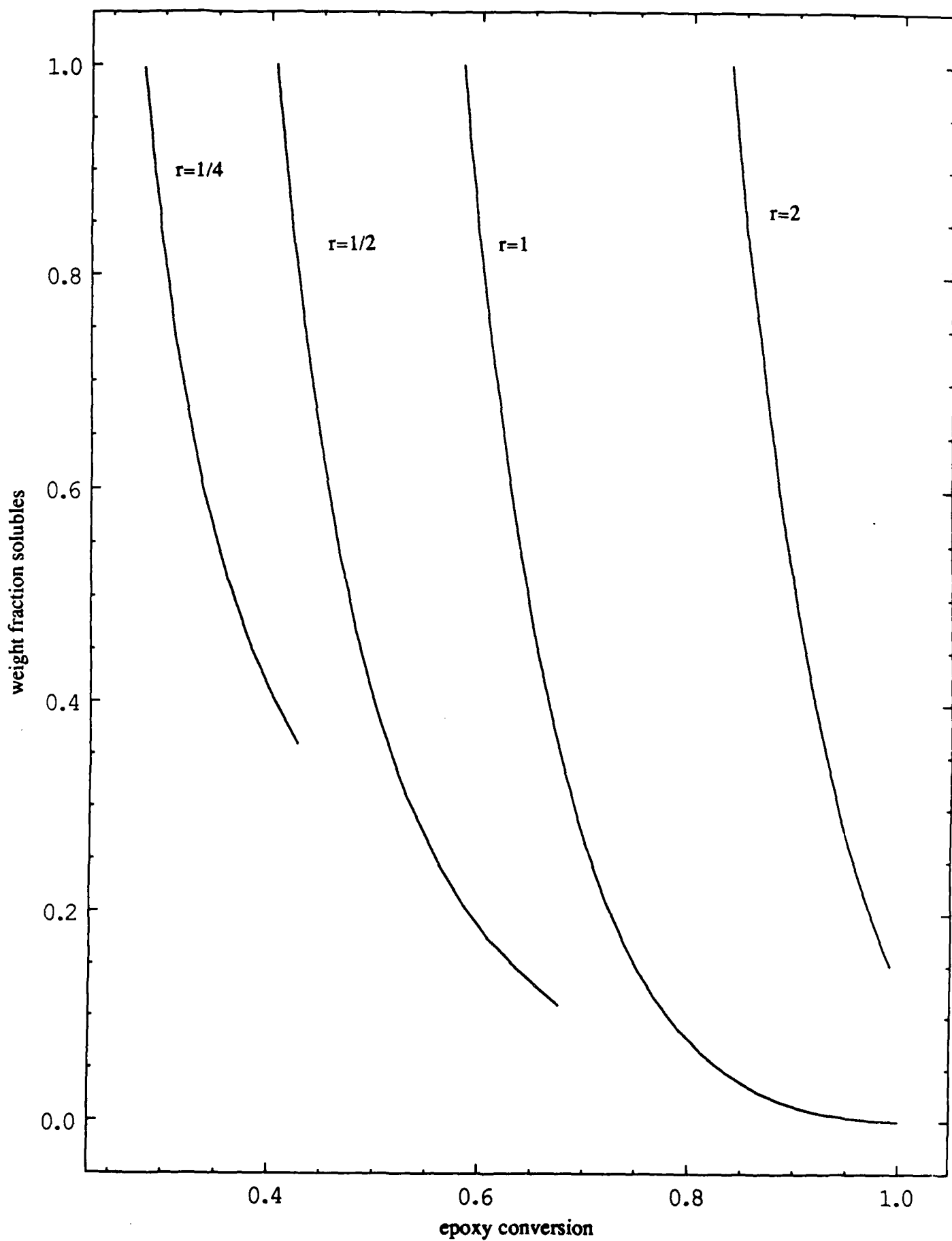
TABLE 1

Conversion of hydrogens at the gel point for different relative rates of etherification
f=4, g=2, r=1.

k_3/k_1	Combined model	Random model	% difference
.001	.58	.58	~0%
.01	.56	.56	~0%
.1	.53	.55	3.8%
1	.39	.47	20%
10	.18	.25	39%
100	.05	.09	80%
1000	.01	.03	200%

TABLE 2

Conversion of amine hydrogens and epoxies at the gel point for different stoichiometric ratios r.
The rate of etherification is 10 times slower than the amine-apoxy addition rate.

r initial stoichiometric ratio	COMBINED MODEL		RANDOM MODEL		% DIFFERENCE	
	hydrogen conversion	epoxy conversion	hydrogen conversion	epoxy conversion	hydrogen conversion	epoxy conversion
1/4	.92	.27	no gelation	no gelation	~	~
1/2	.72	.39	.78	.42	8%	8%
1	.53	.55	.58	.58	4%	5.5%
2	.38	.78	.81	.81	2.7%	4%

TABLE 3

Conversion of amine hydrogens and epoxies at the gel point for different stoichiometric ratios r. The rate of etherification is 10 times faster than the amine-apoxy addition rate. f=4, g=2.

r initial stoichiometric ratio	COMBINED MODEL		RANDOM MODEL		% DIFFERENCE	
	hydrogen conversion	epoxy conversion	hydrogen conversion	epoxy conversion	hydrogen conversion	epoxy conversion
1/4	.28	.19	.47	.53	68%	180%
1/2	.23	.26	.34	.56	48%	115%
1	.18	.35	.25	.63	39%	80%
2	.13	.47	.18	.74	38%	57%